

## Supporting information for

### Liquid Crystal-Based Emulsions for Synthesis of Spherical and Non-Spherical Particles with Chemical Patches

Frédéric Mondiot, Xiaoguang Wang, Juan J. de Pablo, and Nicholas L. Abbott\*

*Department of Chemical and Biological Engineering, University of Wisconsin – Madison, USA*

#### Materials

The liquid crystalline (LC) phase consisted of either pure 4-cyano-4'-pentylbiphenyl (5CB, Merck®) or 5CB containing 20% wt/wt of the reactive mesogenic monomer, 4-(3-acryloyloxypropyloxy) benzoic acid 2-methyl-1,4-phenylene ester (RM257, Merck®) to which the photo initiator 2-dimethoxy-2-phenyl acetophenone (DMPAP, Sigma-Aldrich®) was added at 5% wt/wt based on the mass of RM257. RM257 is crystalline up to ~ 65°C, nematic up to ~ 127°C, and isotropic above 127°C. The aqueous phase was deionized water (resistivity of 18.2 MΩ cm. Deionization of a distilled water source was performed with a Milli-Q system (Millipore, Bedford, MA)) mixed with glycerol at 90% v/v (Sigma-Aldrich®, 99.5% pure) and 1-μm-diameter fluorescent colloids (0.01% wt/v). The colloids were either polystyrene (PS) or silica. Sulfate-terminated fluorescent PS colloids were purchased from Invitrogen ( $\lambda_{exc} = 505$  nm/  $\lambda_{em} = 515$  nm) and used as received. Silica colloids were purchased from Corpuiscular Inc. ( $\lambda_{exc} = 488$  nm/  $\lambda_{em} = 510$  nm). We functionalized the surface of the silica colloids with N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP; 42% in methanol, Sigma-Aldrich®).

#### Methods

##### Preparation of DMOAP-coated silica colloids

The silica colloids (4 mg) were rinsed, centrifuged, and redispersed in 8 mL of deionized water twice. They were then dispersed in 8 mL of 2 M sulfuric acid (Fisher Scientific) and sonicated for 40 minutes. Following sonication, the colloids were centrifuged and redispersed in 8 mL of deionized water twice. They were then stirred vigorously while adding 114.4 μL of DMOAP. Stirring was continued for 25 minutes, at which point the colloids were centrifuged and redispersed in 8 mL of deionized water 4 times. The silica colloids were finally centrifuged and redispersed in 1 mL of deionized water.

##### Preparation of the LC-in-water emulsions

LC-in-water emulsions were prepared by emulsifying 8.8 μL of LC in 4.39 mL of an aqueous phase using a homogenizer T 25 digital ULTRA-TURRAX® equipped with a S25 N - 10 G dispersing element (IKA®), for 30 s at 6,500 rpm. The emulsions were contained in 19-mm-diameter, 51-mm-height glass vials.

##### Photopolymerization of the LC droplets in the LC-in-water emulsions

Photopolymerization of the 5CB/RM257/DMPAP mixture was performed using a UV lamp (365 nm) that delivered 2.5 mW/cm<sup>2</sup>. The emulsions (4.4 mL) were polymerized in a 19-mm-diameter, 51-mm-high glass vial that was exposed to UV light for 40 minutes.

##### Extraction of 5CB from the polymerized LC droplets

After polymerization, 3.5 mL of each emulsion was diluted with 31.5 mL of deionized water. 32 mL of the diluted emulsion then placed into in 16 2-mL polypropylene microcentrifuge tubes (Fisher Scientific), and centrifuged 25 min at 4,100 rpm using a centrifuge 5417R (Eppendorf). The aqueous phase was removed, and 200 μL of ethanol (EtOH) was added to each tube to redisperse the sediment and dissolve 5CB contained in the polymerized particles. Next 3.2 mL of the ethanolic solution was distributed into 2 2-mL

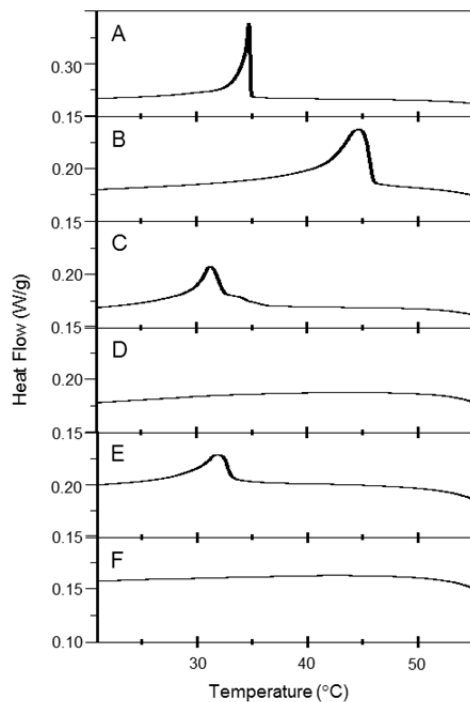
polypropylene microcentrifuge tubes, and 400  $\mu\text{L}$  of EtOH was added to each tube. The solutions were then centrifuged 25 min at 4,100 rpm. EtOH was removed, and 200  $\mu\text{L}$  of fresh EtOH was added again to each tube. The solutions were transferred in a single 2-mL polypropylene microcentrifuge tube, to which was added 1.6 mL of EtOH. They were then centrifuged 25 min at 4,100 rpm, at which point the EtOH was removed and 500  $\mu\text{L}$  of deionized water was added to redisperse the sediment.

### **Bright field (BF), polarized light (PL), and fluorescence (Fluo) microscopy**

The non-polymerized and polymerized droplets were imaged using an Olympus IX71 inverted epifluorescence microscope (Center Valley, PA) equipped with a 100x oil-immersion objective, crossed polarizers, a Hg lamp, and an Olympus U-MNB2 filter ( $470 \text{ nm} \leq \lambda_{\text{exc}} \leq 490 \text{ nm}$ ;  $\lambda_{\text{em}} \geq 520 \text{ nm}$ ) to excite the fluorophore of the colloids. BF, PL, and Fluo micrographs of the LC-in-water emulsions were collected with a Hamamatsu 1394 ORCAER CCD camera (Bridgewater, NJ) connected to a computer and controlled through SimplePCI imaging software (Compix, Inc., Cranberry Twp., NJ). BF micrographs were collected by removing a polarizer from the optical path of the incoming light.

### **Differential scanning calorimetry (DSC)**

DSC characterization was carried out using a DSC Q100 (TA Instruments). The samples were put in hermetic aluminium pans which were sealed. We characterized pure 5CB (Figure S1 A), a mixture of 5CB, RM257 (20% wt/wt) and DMPAP (5% wt/wt based on the mass of RM257) prior to polymerization (Figure S1 B), a polymerized mixture of 5CB, RM257 (20% wt/wt) and DMPAP (5% wt/wt based on the mass of RM257) (Figure S1 C), the polymerized mixture described in C that was extracted with excess EtOH (Figure S1 D), polymerized LC droplets prior to extraction with EtOH (Figure S1 E) and after extraction with EtOH (Figure S1 F). The sample characterized in Figure S1 C and S1 D was obtained by polymerizing 100  $\mu\text{L}$  of the 5CB mixture containing RM257 at 20% wt/wt and DMPAP (5% wt/wt based on the mass of RM257) spread onto a glass slide. After polymerization, the solid material was washed with an excess of EtOH to extract 5CB from the polymer network, and put under vacuum at 60°C overnight to completely evaporate EtOH. The unwashed polymerized LC droplets were first concentrated in deionized water (without glycerol), and, after a centrifugation step to sediment the droplets and remove the water phase, were dried under vacuum at 60°C overnight to completely evaporate last traces of water. The polymerized droplets washed with EtOH were also put under vacuum at 60°C overnight to completely evaporate EtOH.



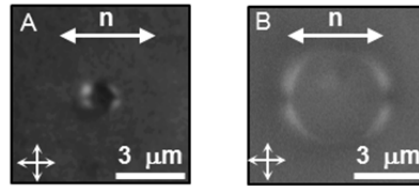
**Figure S1.** DSC characterization of (A) pure 5CB, (B) a mixture of 5CB, RM257 (20% wt/wt) and DMPAP (5% wt/wt based on the mass of RM257) prior to polymerization, (C) the mixture described in B after polymerization, (D) the material described in C after extraction with EtOH, (E) polymerized LC droplets prior to extraction with EtOH, and (F) polymerized LC droplets after extraction with EtOH.

**Table S1.**  $T_{NI}$  deduced from the DSC measurements. The letters refer to those in Figure S1.

Material	$T_{NI}$ (°C)
(A) Pure 5CB	35
(B) Mixture containing 5CB, RM257 (20% wt/wt) and DMPAP (5% wt/wt based on the mass of RM257), prior to polymerization.	46.1
(C) Mixture in B after polymerization.	33
(D) Mixture in C after extraction with EtOH.	
(E) Polymerized LC droplets prior to extraction with EtOH.	33
(F) Polymerized droplets in E after extraction with EtOH.	

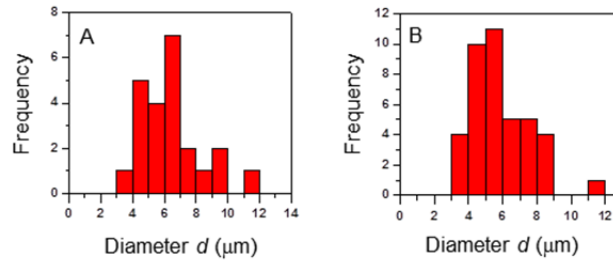
### Optical characterization of the anchoring of LC on sulfate-terminated PS colloids

We used optical microscopy (crossed-polars, transmission mode) to characterize the nematic LC orientation around sulfate-terminated PS colloids dispersed in nematic 5CB to determine how 5CB molecules orient/anchor at the colloid surface. Both 1- $\mu\text{m}$ -diameter and 4- $\mu\text{m}$ -diameter, sulfate-terminated PS colloids (from the same manufacturer), as shown on Figure S2 A and B, respectively, induce elastic distortions (bright regions in Figure S2) of the surrounding nematic that have a quadrupolar symmetry. The quadrupolar pattern of the distortions is consistent with an orientation/anchoring of the 5CB molecules that is parallel/tangential to the colloid surface.<sup>2</sup>



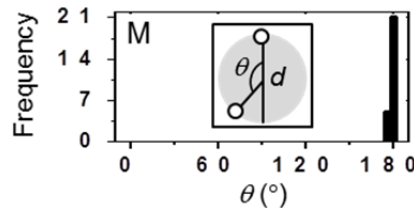
**Figure S2** – PL micrographs of (A) a 1- $\mu\text{m}$ -diameter, sulfate-terminated PS colloid, and (B) a 4- $\mu\text{m}$ -diameter, sulfate-terminated PS colloid dispersed in nematic 5CB. The bright regions correspond to elastic distortions of the nematic director field at the colloid surface which are consistent with planar anchoring.<sup>1</sup>

### Size distributions of the 5CB droplets with either one or two PS colloids adsorbed on their surfaces



**Figure S3** – Diameters of 5CB droplets exhibiting either (A) a single PS colloid or (B) two PS colloids adsorbed at their surfaces.

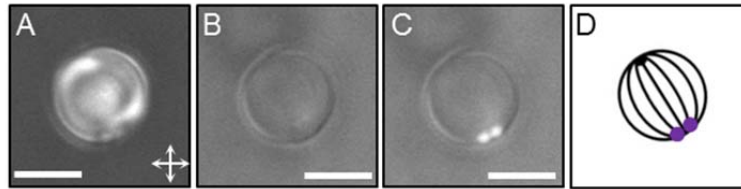
### Distribution of angles measured between pairs of PS colloids adsorbed at the surfaces of 5CB droplets (from the population of 5CB droplets shown in Figure S2 B).



**Figure S4** – Distribution of angles ( $\theta$ , see inset) defined by pairs of PS colloids adsorbed to droplets of 5CB (with sizes characterized in Figure S3 B).

### Optical characterization of 5CB droplets with two PS colloids at a single pole

As stated in the main text, we also observed bipolar 5CB droplets with two colloids located at a single pole of the droplets (Figure S5).



**Figure S5** – (A) PL, (B) BF, and (C) combined Fluo and BF micrographs of a bipolar nematic 5CB droplet observed in a water/glycerol (90% v/v) mixture, with a diameter of 6.5  $\mu\text{m}$ , and exhibiting two PS colloids adsorbed at its surface (bright spots in C). Scale bars: 5 $\mu\text{m}$ . (D) The corresponding illustration of the director field configuration (dark lines) with the two “boojum” defects at the droplet poles; the purple spots represents the PS colloids (that appear to “share” the defect at the pole).

### Reference

1. Poulin, P.; Weitz, D. A. *Phys. Rev. E* **1998**, 57, 626-637.